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RESEARCH ARTICLE

A SELECTIVE FE^{3+} FLUORESCENT PROBE DERIVED FROM NAPHTHALIMIDE

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ABSTRACT

In this work, a new fluorescent probe P based on naphthalimide was constructed to detect Fe^{3+} over other metal ions. The addition of Fe^{3+} to the solution of P caused an obvious fluorescent quenching at 400 nm.

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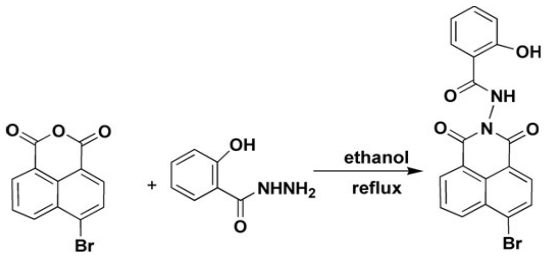
INTRODUCTION

The fluorescence probe is based on the organic combination of molecular recognition and fluorescence technology, and realizes molecular recognition through specific receptor binding targets, and then converts the information into fluorescence signals that are easy to detect through the corresponding fluorescence signal transduction mechanism, so as to achieve in-situ and real-time detection at the single molecule level (1). With the rapid development of fluorescence probe technology in recent years, the research of this method in the detection of heavy metal ions in the environment, cells and organisms has made great progress (2-5). A new fluorescence probe with fast response, good selectivity, high sensitivity and good biocompatibility has been designed and synthesized to achieve the detection of target metal ions, and it is expected to obtain a probe with excellent performance, and further expand the work to explore the fluorescence imaging analysis of intracellular metal ions. Naphthalimide derivatives are a class of fluorescence emitting groups with coplanar rigidity and large conjugated systems, which have excellent properties such as optical properties, large Stokes shift, high fluorescence quantum yield, and strong chemical modifiability (6,7). The diversity of naphthalimide fluorescent probes was studied by modifying different compound groups for specific detection or connecting another fluorophore for ratio detection. In recent years, different sites of naphthalimide molecules have been modified to change their fluorescence properties and form conjugated systems of electron-withdrawing or electron-donating groups (8-10).

Tian synthesized a fluorescent probe based on naphthalimide fluorophore to specifically identify Hg^{2+} (11). Wang synthesized a fluorescence-enhanced Al^{3+} probe based on naphthalimide derivatives, which could be applied to the detection of Al^{3+} in real environmental water samples (12). In view of the excellent performance of such naphthalimide probes, this project independently designed and synthesized a new type of fluorescent probe based on naphthalimide derivatives to promote the effective implementation of environmental testing and governance. The synthesis route was shown in scheme 1.



Scheme 1 The synthesis route of P.

EXPERIMENTAL SECTION

Reagents and Instruments: The metallic salt used in the experiment are from NaCl, $MgCl_2 \cdot 6H_2O$, $CdCl_2$, $HgCl_2$, $CaCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $AgNO_3$, $CoCl_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, and $PbCl_2$, respectively. Fluorescence emission spectra were conducted on a Hitachi4600 spectrofluorometer.

Synthesis of probe P: Under N_2, 0.0277 g (0.1mmol) of 4-bromo-1, 8-naphthalene anhydride and 0.0182 g (0.12 mmol) of salicylhydrazide were added to a 100 mL three necked bottle containing 30 mL of ethanol, the reaction mixture was reacted for 6 h and then cooled to room temperature. The yellow precipitate produced was filtered and used directly.

Test conditions: The excitation wavelength of fluorescence measurement was 350 nm, the slits of excitation and emission wavelength were both of 10 nm. The concentration of probe P was 10 μM in DMSO and the test medium was ethanol.

RESULTS AND DISCUSSION

Selectivity measurement of P: To further investigate the selectivity of the fluorescent probe, fluorescence measurements were carried out toward various metal ions by using the excitation wavelength 350 nm of naphthalimide fluorophore. As expected, P exhibited excellent selectivity for Fe^{3+} at 400 nm over alkali and alkaline-earth metal ions (Figure 1). These ions including Hg^{2+}, Co^{2+} had an enhanced effect on the signal. These facts indicated that P was a good candidate that recognized Fe^{3+}.

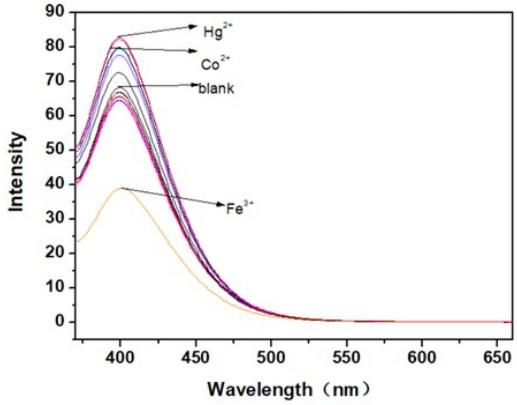


Figure 1. Effects of different metal ions (100 μM) (Hg^{2+}、Ni^{2+}、Cu^{2+}、Co^{2+}、Ca^{2+}、Na^{+}、K^{+}、Zn^{2+}、Mg^{2+}、Ba^{2+}、Pb^{2+}、Cd^{2+}、Fe^{3+}) on the fluorescence spectra of probe P (10 μM) in ethanol at 350 nm excitation wavelength

Sensitivity measurement of P: Additionally, for different amounts of Fe^{3+} (0-10 μM), the intensity of the fluorescent peak at 400 nm gradually decreased (Figure 2). We believe that this may be due to the paramagnetic nature of Fe^{3+} itself, which often leads to fluorescence quenching.

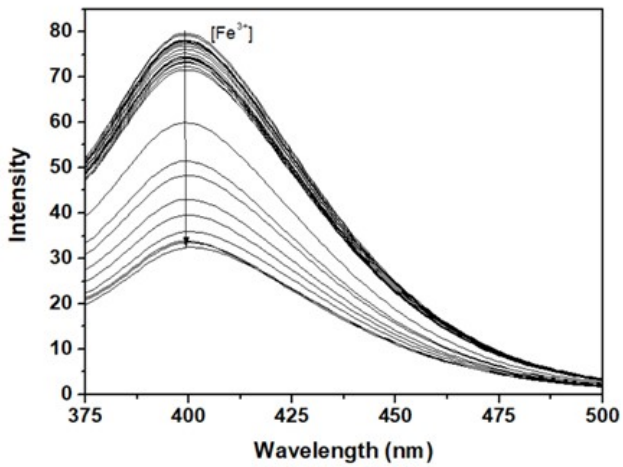


Figure 2. Effect of Fe^{3+} (0-10 μM) concentration on the fluorescence spectrum of probe P (10 μM)

Competitive effects of Fe^{3+}: Further investigation was conducted on the competitive effects of common metal ions coexisting in P-Fe^{3+} system, the results were shown in Figure 3. Under the same conditions, the presence of Hg^{2+} can affect the fluorescence intensity of the probe, others did not interfere significantly. Therefore, it was determined that probe P still can be applied in the environmental sample.

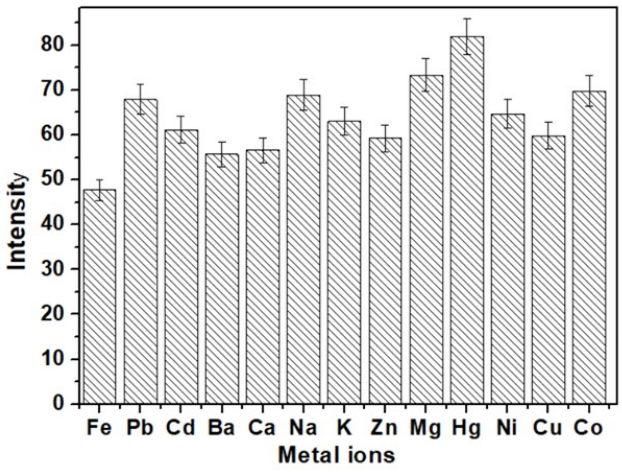


Figure 3. Fluorescence response of P (10 μM) to Fe^{3+} (10 μM) or to a mixture of the specified metal ions (50 μM) with Fe^{3+} (10 μM) in ethanol

Reversibility of P-Fe^{3+} system: As shown in Figure 4, the reversibility of P-Fe^{3+} system was investigated. Only probe P displayed the obvious fluorescence intensity at 400 nm (Fig. 5a). After Fe^{3+} was added, the fluorescence intensity decreased (Fig. 5b). After the addition of EDTA, the fluorescence intensity at 400 nm of the system was somewhat enhanced due to the competition effect (Fig. 5c-d). When excessive Fe^{3+} was added to combine with the probe, the fluorescence intensity at 400 nm was also quenched (Fig. 5e-f), which proved that the probe had a certain reversibility.

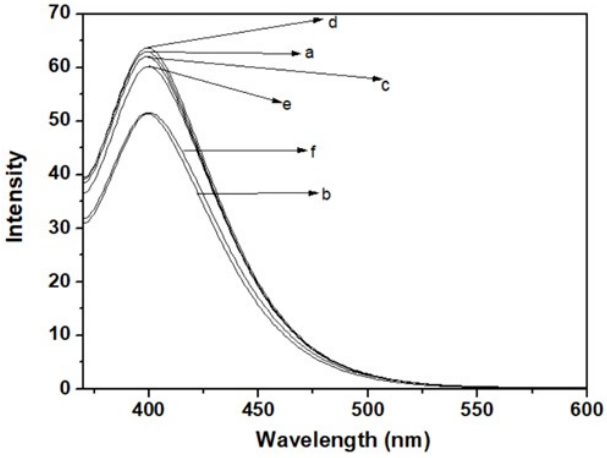


Figure 4. The reversibility of the probe P-Fe^{3+} system in the ethanol. a. P (10 μM); b. P (10 μM) + Fe^{3+}(10 μM); c. P (10 μM) + Fe^{3+}(10 μM) + EDTA (10 μM); d. P (10 μM) + Fe^{3+}(10 μM) + EDTA (50 μM); e. P (10 μM) + Fe^{3+}(10 μM) + EDTA (50 μM) + Fe^{3+}(50 μM); f. P (10 μM) + Fe^{3+}(10 μM) + EDTA (50 μM) + Fe^{3+}(100 μM).

CONCLUSION

In summary, it can be seen that the probe had a clear recognition for Fe^{3+}. With the increasing of Fe^{3+} concentration within the range of 1-10 μM, the fluorescence intensity at 400 nm decreased regularly. Meanwhile, through coexisting ion competition experiments, the probe displayed the potential to be applied in complex samples

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